PATENT SPECIFICATION

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(54) DEHYDRATION PROCESS

(71) We, COMPAGNIE FRANCAISE DE RAFFINAGE, a French Body Corporate of 5, rue Michel Ange-75116 Paris, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the dehydration of organic compounds. More particularly, it relates to a process for the dehydration of vicinal diols and/or olefinic alcohols.

The description which follows deals, more particularly, with the application of certain catalysts to the dehydration of methyl-2,3-butanediol because of the importance which it has assumed. As is known, the dehydration of methyl-2,3-butanediol leads to isoprene, a monomer that is very much in demand for the manufacture of both synthetic rubbers and a wide range of high polymers. However, this particular application should not be construed as a limitaton of the invention, which may be applied to other compounds as well—for example, to the dehydration of 2,3-butanediol to give butadiene.

The usual dehydration catalysts, such as thoria or alumina, cannot be used in the dehydration of methyl-2,3-butanediol or of vicinal diols generally. They result in excessive amounts of by-products such as methyl isopropyl ketone and trimethyl acetaldehyde or, more generally, carbonyl compounds. On the other hand, the application of lithium orthophosphate, Li_3PO_4, which is known to be a catalyst for the isomerization and dehydration of 2-methylepoxy-2,3-butane to isoprene, in the dehydration of methyl-2,3-butanediol gives only a low isoprene yield when the lithium phosphate is prepared without special precautions.

In our Patent Specification No. 1,355,705 there is described and claimed a method of preparing a dehydration catalyst comprising at least one neutral pyrophosphate of at least one metal selected from lithium, sodium, strontium and barium, which method comprises mixing at least one neutral pyrophosphate of at least one metal selected from lithium, sodium, strontium and barium with at least one acid orthophosphate of at least one metal selected from lithium, sodium, strontium and barium, forming an extrudate from the resulting mixture and thereafter drying and calcining the extrudate in air in order to convert the acid orthophosphate into neutral pyrophosphate.

Our Patent Specification No. 1,355,704 describes and claims a process for dehydrating a diol to provide a diolefin and/or an olefinically unsaturated alcohol, which process comprises contacting the diol under dehydrating reaction conditions, wth a dehydration catalyst which comprises at least one neutral pyrophosphate of at least one metal selected from lithium, sodium, strontium and barium.

These catalysts have proved particularly effective and worthwhile in the dehydration of metal-2,3-butanediol to isoprene and/or to olefinic alcohols, which are intermediate products in the dehydration of methyl-2,3-butanediol to isoprene.

An object of the present invention is to provide a dehydration process, particularly for vicinal diols, using a catalyst which is as selective and as active as the catalysts mentioned above, and preferably using less expensive starting materials.

In pursuing their investigations, the applicants have found that solids based on calcium pyrophosphate also make very good catalysts for dehydration, especially of diols to dienes, specifically including vicinal diols.

According to the present invention there is provided a process for the catalytic dehydration of vicinal diols and/or olefinic alcohols to diolefins and/or olefinic alcohols which process comprises carrying out the dehydration in the presence of a catalyst consisting of calcium pyrophosphate alone or a catalyst composition comprsing (i) calcium pyrophosphate, and (ii) at least one pyrophosphate, whether mixed or

not, of at least one of lithium, sodium, strontium and barium, and/or at least one neutral orthophosphate, wether mixed or not, or at least one of lithium, sodium, strontium, barium and calcium.

The applicants have found that these calcium-based catalysts are as advantageous as the catalysts discovered earlier. A further advantage is that the calcium-based compounds — for example, calcium chloride, $CaCl_2$ — necessary for the manufacture of the catalyst are cheaper than lithium-based compounds, for example, and this translates into a substantial cost saving.

The applicants have found, moreover, that calcium-based catalysts exhibit better thermal stability than the catalysts used up to now. When used alone, calcium pyrophosphate has a melting point of about 1300° C. When used in admixture with another pyrophosphate, the catalysts obtained will not undergo a deleterious thermal change until an elevated temperature is reached. For example, when a calcium pyrophosphate is used in admixture with sodium pyrophosphate prepared from sodium acid orthophosphate, the catalytic mass obtained will not undergo a thermal change up to 780° C., which is approximately the melting temperature of sodium pyrophosphate. In the course of their work, the applicants have further found that the thermal degradation which occurs manifests itself in a frittering of the catalyst, and this shortens its service cycle. Moreover, since these catalysts are employed mainly in the dehydration of diols to diolefins, the diolefins produced may polymerize on the catalyst. It follows that to regenerate the catalyst the latter has to be brought to an elevated temperature to burn off the polymers deposited on its surface, which quite often have already been converted to coke. A catalyst based on calcium pyrophosphate therefore undergoes less alteration during regeneration than other catalysts since the temperature at which it begins to sustain a thermal chance is higher than that at which other catalysts undergo alteration.

However, when used alone, calcium pyrophosphate has rather mediocre mechanical properties for a catalyst. It is therefore preferable to mix it with a pyrophosphate, whether mixed or not, of at least one of the metals of the group consisting of lithium, sodium, strontium and barium, obtained from the corresponding acid orthophosphate. For example, the calcium pyrophosphate may be mixed with sodium acid orthophosphate, which then is converted to neutral pyrophosphate.

Several processes for the preparation of calcium pyrophosphate are known. One of these is the so-called "dry" route whereby the pyrophosphate is obtained by calcination of mixtures of salts of calcium, such as the oxide, CaO, the hydroxide, $Ca(OH_2)$, the carbonate, $CaCO_3$, and so forth, and of phosphoric acid (ammonium phosphate, phosphoric acid, etc.). For example, the applicants have run tests with ammonium phosphate and calcium carbonate.

Another of these processes might be called the "wet" route. Calcium pyrophosphate being insoluble in water, it may be precipitated by double decomposition between a solution of calcium salt and a solution of a pyrophosphate. The starting materials may be an inorganic or organic calcium salt, for example, the chloride or the acetate of calcium, and sodium pyrophosphate, $Na_4P_2O_7 . 10H_2O$; calcium pyrophosphate, $Ca_2P_2O_7$ thus being precipitated.

Lastly, still another possible route is the calcination of the phosphate $CaHPO_4$, which may be preceded by the precipitation of the dicalcium orthophosphate.

However, the applicants have found in the course of their tests that the calcium pyrophosphate produced by the "dry" route is a compact, scarcely divided, often heterogenous solid. The porosity therefore is low, which is detrimental for a dehydration catalyst. The other two methods, on the other hand, yield solids which hold promise for the manufacture of catalysts.

To improve the mechanical properties of the catalyst, the applicants prefer to employ the process of preparation described in what follows. The process consists in mixing calcium pyrophosphate, prepared either by the "wet" route or by calcination of dicalcium orthophosphate, with disodium acid orthophosphate, for example; extruding or pelletizing the mixture so obtained; drying it at about 100 or 120° C.; and calcining it so as to convert the acid orthophosphate to pyrophosphate. To facilitate the mixing of the powders, water (from 0 to 150% of the total weight of the powders) may be added. Of course, if one of the powders is sufficiently moist, there will be no need to add water during mixing. However, water must be added if the powders are dry. In fact, a paste must be obtained which then is dried, ground, screened and pelletized. The catalyst so produced has good mechanical properties in addition to good catalytic properties. Good catalysts are obtained also by mixing or coprecipitating calcium pyrophosphate, and possibly at least one neutral orthophosphate of at least one metal from the group consisting of lithium, sodium, strontium, barium and calcium, with at least one pyrophosphate, whether mixed or not, of at least one metal from the group consisting of lithium, sodium, strontium and barium. The neutral orthophosphate acts as a bonding agent which improves the mechanical properties of the catalysts, and particularly its resistance to crushing, without affecting its original catalytc properties.

In all of the mixtures referred to above, the calcium pyrophosphate is preferably present in a proportion of from 40 to 80 wt. %.

The catalytic dehydration of diols, whether

vicinal or not, may be effected either in the liquid state or in the vapor state. However, it is preferably carried out in the vapor phase and at a temperature comprised between 250 and 600° C., and preferably between 300 and 500° C., and a space velocity per hour (v/v/hr)—which specifies the volume of diol, measured in the liquid state, passing over a unit volume of catalyst in one hour—generally comprising between 0.1 and 5, and preferably between 0.5 and 2.5 v/v/hr.

The diol may be pure or diluted in an inert gas such as nitrogen, or mixed with olefinic alcohols. The dehydration of the diol directly to diene is carried out with production of intermediates such as the aforesaid olefinic alcohols, which essentially are β-olefinic alchols. For example, in the dehydration of methyl-2,3-butanediol, 2-methyl-1-butene-3-ol is formed which may readily be recycled in the dehydration reactor, since the catalysts used in the process in accordance with the invention will dehydrate said olefinic alcohols just as effectively to dienes.

A catalyst used in the process in accordance with the invention may be employed industrially in one or more dehydration reactors in the manner which is well known in the field of catalytic reactions. However, the catalyst is preferably used in a fixed bed.

The examples which follow are in no wise limitative. They relate to the preparation of the catalysts and their application to the dehydration of a diol to diene.

EXAMPLE I.

This example relates to the preparation of pure calcium pyrophosphate. 200 cc of a solution containing 31.6 g of $(CH_3COO)_2Ca$ is poured into a solution of 100 cc of $Na_4P_2O_7 \cdot 10H_2O$ containing 44.7 g of that salt. The solutions are hot. A precipitate of calcium pyrophosphate is obtained which is filtered, washed, and dried at 110° C.

The preciptate is calcined in two portions. One portion is calcined at 500° C. for 2 hours while the other portions is calcined at 725° C., also for 2 hours.

Conventional macroporosity and apparent-density measurements are then made on the two portions of catalyst. The results thereof are presented in Table I below.

The catalytic tests are carried out as follows: Methyl-2,3-butanediol carried by a nitrogen stream is passed over 4.5 cc of catalyst at 1 v/v/hr.

The results of the catalytic tests are also presented in Table I. It should be noted that the calcium pyrophosphate here used is in the form of a powder which has good activity and good selectivity but would be difficult to use on an industrial scale.

TABLE I

Temperature of calcination of $Ca_2P_2O_7$	PHYSICAL PROPERTIES		CATALYTIC TEST 400°C – 1 v/v/hr					
				Product distribution in mole per cent in the converted fraction				
	Macro porosity cc/g	Apparent density g/cc	Conversion	Isoprene	Olefinic alcohols	Carbonyl compounds	Misc.	Selectivity
500°C	3.03	0.17 (powder)	100	44.4	40.3	14.3	0.9	85.2
725°C	2.47	0.20 (powder)	87.6	23.8	59.8	12.0	4.3	85.3

In that Table—

—the conversion represents the ratio of number of molecules of diol consumed to number of molecules of diol introduced;

—the selectivity is equal to the sum of the mole percentages, in the converted fraction, of isoprene and isoprene precursors (mainly the olefinic alcohols produced along with the isoprene but also, to a small extent, 2-methyl-epoxy-2,3-butane); and

—the macroporosity of the catalysts designates, in cc/g, the pore volume of one gram of catalyst for pores having a radius comprised between 80 and 100 Å and 75000 Å. It is determined by means of a well-known apparatus, the mercury penetration porosimeter.

It is apparent that raising the temperature of calcination has a deleterious effect on diene production, as for a temperature increase of about 200° C. the mole percentage of isoprene, the desired diene, is roughly halved.

EXAMPLE II.

In this example, the same method of preparation is employed as in Example I, but only up to the drying step. A calcium pyrophosphate that has been dried at 110° is then at hand.

To 52 g of dried precipate, 34.7 g of decahydrated disodium phosphate, $Na_2HPO_4 . 10H_2O$ weight ratio, 60%:40%), is added, and then 87 cc of water to form the paste, which is dried at 120° C., ground, and screened so that only particles of a size comprised between 0.5 an 1 mm are retained for the catalytic test. Lastly, these particles are calcined for 2 hours at 500° C. In the course of this operation, the water present in the catalytic particles is eliminated and the disodium orthophohphate is converted to sodium pyrophosphate. The catalyst so prepared has a macroporosity of 0.876 cc/g and an apparent density of 0.46 g/cc.

Theree catalytic tests are then made which consist in passing methyl-2,3-butanediol in the vapor phase at 1 v/v/hr over 4.5 cc of catalyst as in Example I. Three tests are run at different temperatures (350, 400 and 450° C., respectively), the results of which are reported in Table II.

TABLE II

		CATALYTIC TEST 1 v/v/hr				
Test temp.	Conversion	Isoprene	Olefinic alcohols	Carbonyl compounds	Misc.	Selectivity
350°C	77.7	16.4	68.4	12.6	3.1	85.5
400°C	100	79.2	2.6	15.0	3.3	81.8
450°C	100	81.1	0.1	15.8	3.0	81.2

It is apparent from this table that catalysts containing calcium pyrophosphate and sodium pyrophosphate are good dehydration catalysts. Above 400° C., the mole percentage of isoprene is substantial, being nearly 80% in relation to the diol converted (and hence to the diol entering, as conversion is 100%).

EXAMPLE III.

In this example, two hot solutions (about 90° C.) are used as starting materials, one of 446 grams/liter of the pyrophosphate $Na_4P_2O_7 . 10H_2O$ (a molar solution), the other of 22 grams/liter of calcium chloride. (hence a 2x molar solution), both in distilled water. The latter solution is poured into the former with agitation. It is found that calcium pyrophosphate precipitates in accordance with the reaction.

$$2CaCl_2 + Na_4P_2O_7 \rightarrow \underset{\downarrow}{\underline{Ca_2P_2O_7}} + 4NaCl$$

The precipitate obtained is filtered and washed with 5 liters of distilled water and then dried at about 110° C. 302.3 grams of a solid having the approximate formula $Ca_2P_2O_7 . 3H_2O$ is obtained.

298.7 g of this precipitate and 128 g of disodium acid orthophosphate,

$$Na_2HPO_4 . 10H_2O,$$

are mixed in a weight ratio of 70:30% with the addition of 395 cc of water so as to facilitate mixing in the form of a paste. The paste is dried at 110° C., followed by grinding and screening so as to retain only particles of a size comprised between 0.5 and 1 mm. The catalyst so obtained has a macroporosity of 1.177 cc/g and an apparent density of 0.37 g/cc. In this operation, the fine particles may be recovered with water, redried and reground.

A catalytic test is performed in accordance with example 1 or 2 at 400° C., methyl-2,3-butanediol being passed over the catalyst at 1 v/v/hr. Conversion of the diol is 98.1%. The molar distribution in the converted fraction is as follows:

Isoprene	51.4%
Olefinic alcohols	28.3%
Carbonyl compounds	16.6%
Miscellaneous	3.7%

The selectivity is 80.2%.

EXAMPLE IV.

The procedure used in Example III is followed in preparing the catalyst, except that here potassium pyrophosphate is used to precipitate the calcium salt:

$$K_4P_2O_7 + 2CaCl_2 \rightarrow \underset{\downarrow}{\underline{Ca_2P_2O_7}} + 4KCl$$

Two cold solutions, one containing 33 g of potassium pyrophosphate per 100 cc of distilled water, the other containing 22.2 g of calcium chloride per 100 cc of distilled water, are mixed. Calcium pyrophosphate is thus precipitated, and the precipitate is filtered and washed with 500 cc of water and then dried at 100° C.

12 g of the dried precipitate is then mixed with 8 g of disodium acid orthophosphate (weight ratio, 60:40%) with the addition of 25 cc of water. The paste obtained, dried at about 120° C., is ground and screened to separate the particles between 0.5 and 1 mm. The particles separated by screening are then calcined at 500° C. for 2 hours.

The catalyst so obtained has a macroporosity of 0.698 cc/g and an apparent density of 0.51 g/cc.

A catalytic test comparable in all respects to that of Example II is then made. The results are as follows:

Diol conversion	98.8%

Product distribution (mole percentages) in the converted fraction:

Isoprene	53.2%
Olefinic alcohols	28.5%
Carbonyl compounds	13.3%
Miscellaneous	4.9%

The selectivity is 82.5%.

In this example, potassium pyrophosphate was used in the preparation of the catalyst. This pyrophosphate offers the advantage of being far more readily soluble than sodium pyrophosphate, whose solubility in water is not pronounced below 80° C. The calcium pyhophosphate may therefore be precipitated cold.

EXAMPLE V.

Calcium pyrophosphate is prepared in the same manner as in Example III. However, the weight ratio of the calcium pyrophosphate and the disodium acid orthophosphate used in the preparation of the catalyst is 50:50%.

The catalytic mass obtained after drying is subjected to two mechanical treatments, namely:

The first portion is pelletized in admixture with 5% of didecyl adiphate and 5% of naphthalene, used as lubricants. The pellets are calcined in a nitrogen stream at 500° C. The catalyst so produced has a macroporosity of 0.266 cc/g and an apparent density of 0.99 g/cc.

The second portion is ground and screened to give granules of a size comprised between 0.5 and 1 mm and is then calcined in a nitrogen stream at 500° C. The catalyst so produced has a macroporosity of 0.344 cc/g and an apparent density of 0.78 g/cc.

TABLE III

		CATALYTIC TEST 400°C – 1 v./v./hr				
Catalyst	Conversion	Isoprene	Olefinic alcohols	Carbonyl compounds	Misc.	Selectivity
Pelletized	100	81.8	0.9	14.7	2.7	82.7
Granulated	95.3	40.5	41.2	14.3	3.9	82.5

EXAMPLE VI.

In this example, calcium pyrophosphate is prepared by calcination of dicalcium orthophosphate, $CaHPO_4$.

First $CaHPO_4$ is prepared by precipitation. To an 0.1 N acid solution of calcium chloride, a solution of diammonium phosphate is gradually added, the operation being performed cold. This preparation is described in "Nouveau Traite de Chimie Minerale", by P. Pascal, on page 462 of volume IV. The precipitate obtained, which is washed with water and dried at 110° C., is identified by its powder pattern. It is dicalcium orthophosphate,

$CaHPO_4 . 2H_2O$.

50.9 g of this precipitate is mixed with 39.4 g of $Na_2HPO_4 . 10H_2O$ with the addition of 120 ml of water. (Weight ratio, 56.3:43.7%). The paste obtained is dried at about 120° C., ground, and screened to give a particle size between 0.5 and 1 mm. This is followed by calcination for 2 hours at 500° C., which converts the orthophosphate $CaHPO_4 . 2H_2O$ to calcium pyrophosphate and the phosphate $Na_2HPO_4 . 10H_2O$ to sodium pyrophosphate.

A test is then run which is identical to those of Example V. The results obtained are as follows:

Diol conversion	99.1%
Molar distribution:	
Isoprene	78.8%
Olefinic alcohols	3.9%
Carbonyl compounds	15.1%
Miscellaneous	1.6%

The selectivity is 83.3%.

Thus the catalyst so prepared is a very good catalyst for the dehydration of diols and olefinic alcohols to dienes.

EXAMPLE VII.

In this example, calcium pyrophosphate is prepared by calcination of dicalcium orthophosphate, $CaHPO_4$, obtained by precipitation from a mixture of calcium chloride and diammonium phosphate by the method described in Example VI. The dicalcium orthophosphate precipiate is dried at 110° C.

A portion of the precipitate is calcined at 500° C. for 2 hours for the purpose of analysis. It is found that the weight per cent of the calcium (32.5, as determined by atomic absorption) and of the phosphorus (23.7, as determined by x-ray fluorescence) correspond to an atomic ratio of calcium to phosphorus of 1.06, which confirms that during calcination dicalcium phosphate, $CaHPO_4$, readily converts to pyrophosphate, $Ca_2P_2O_7$.

Another portion of the dried precipitate is mixed with disodium orthophosphate in a weight ratio of 50:50%. The paste obtained is ground and screened so as to retain for the catalytic test only particles of a size between 0.5 and 1 mm. These particles are calcined at 500° C. for 2 hours. The catalyst ultimately obtained has a macroporosity of 1.313 cc/g

and an apparent density of 0.36 g/cc. A catalytic test is then run with methyl-2,3-butanediol as in the preceding examples (at 350° C. and 1 v/v/hr). Conversion of the diol is 84.6%.

The molar distribution in the converted fraction is as follows:

Isoprene	42.7%
Olefinic alcohols	41.9%
Carbonyl compounds	12.7%
Miscellaneous	2.6%

EXAMPLE VIII.

Described in this example is the use of a catalyst prepared from the following mixture:

25 wt. % of calcium pyrophosphate, $Ca_2P_2O_7$
25 wt. % of mixed pyrophosphate, $Li_2NaP_2O_7$
50 wt. % of acid orthophosphate,
$Na_2HPO_4 . OH_2O$

This mixture is prepared in the form of a paste which is treated to give catalyst granules that are dried overnight at 75° C. and calcined for 2 hours at 400° C. The catalyst so obtained has a macroporosity of 1.088 cc/g and an apparent density of 0.365 g/cc.

Methyl-2,3-butanediol is then dehydrated over this catalyst at 350° C. and 1 v/v/hr by the procedure described in the preceding examples. Diol conversion is 36.9%. The molar distribution in the converted fraction is as follows:

Isoprene	10.2%
Olefinic alcohols	73.8%
Carbonyl compounds	13.6%
Miscellaneous	2.4%

The selectivity (84%) is good. Conversion, on the other hand, is low but can readily be increased by reducing the space velocity per hour or by raising the test temperature, and this does not constitute a limitation of the catalyst so prepared. It is also seen that the mole percentage of olefinic alcohols is high, but this is not a drawback as they can be recycled over the catalyst, which then will dehydrate them to isoprene.

EXAMPLE IX.

This example relates to the simultaneous preparation of calcium pyrophosphate and tricalcium orthophosphate. A mixture of calcium chloride (½ mole) and disodium acid orthophosphate, $Na_2HPO_4 . 10H_2O$ (1 mole), is the starting material. The procedure used in the preceding examples is followed. (A solution containing ½ mole of $CaCl_2$ and a soluton containing 1 mole of $Na_2HPO_4 . 10H_2O$ are mixed.) In this way, a solid is precipitated which is dried overnight at 75° C. and then calcined for 2 hours at 400° C.

An analysis made of the dried precipitate (by atomic absorption in the case of the calcium and by x-ray fluorescence for the phosphorus) gives 32.1 wt. % of calcium and 18.5 wt. % of phosphorus. The atomic ratio of Ca/P thus is 1.35, which places it between that of pyrophosphate (for which this ratio is 1) and that of tricalcium phosphate, $Ca_3(PO_4)_2$ (for which the ratio is 1.5). The x-ray diagram of the solid shows that these two constituents are present in the solid obtained by calcination, which gives good results in the dehydration of 2-methyl-2,3-butanediol, carried out as in the preceding examples (at 350° C. and 1 v/v/hr). Conversion of the diol is 100%, and the molar distribution in the converted fraction is as follows:

Isoprene	69.7%
Olefinic alcohols	0%
Carbonyl compounds	29.7%
Miscelleneous	0.6%

The catalyst prepared and used in this test has a macroporosity of 1.46 cc/g and an apparent density of 0.315 g/cc.

Another test run with a catalyst prepared from 0.8 mole of calcium chloride and 1 mole of disodium orthophosphate under the same conditions as the one above, and which upon analysis was found to contain 37% of calcium and 20.6% of phosphorus, which corresponds to an atomic ratio of Ca/P of 1.39, gave the following results:

Diol conversion	100%
Molar distribution:	
Isoprene	69.7%
Olefinic alcohols	15.3%
Carbonyl compounds	13.5%
Miscellaneous	1.5%

The catalyst used in this test has a macroporosity of 0.812 cc/g and an apparent density of 0.455 g/cc.

Thus the above two catalysts, formed of calcium pyrophosphate and tricalcium orthophosphate, are equally good catalysts for the dehydration of diols to dienes and/or olefinic alcohols.

EXAMPLE X.

This example relates to a dehydration test on 2-methyl-2,3-butanediol with a magnesium pyrophosphate as catalyst.

More precisely, this test is intended to show that not every alkaline-earth metal is suited for dehydration of a vicinal diol and/or of olefinic alcohols to diolefins and/or olefinic alcohols.

Two identical tests are run in parallel over 5 cc each of catalyst, one a calcium pyrophosphate catalyst, the other a magnesium pyrophosphate catalyst. The methyl butanediol is introduced over the catalysts in the presence

of nitrogen (in a ratio of $\frac{1}{3}$ diol to $\frac{2}{3}$ nitrogen) at 400° C. and 1 v/v/hr (measured in the liquid state). The test duration is 1 hour. The results are summarized in Table IV.

TABLE IV

Catalyst used	Selectivity %	Activity mole/g hr*
Calcium pyrophosphate	85.3	0.0644
Magnesium pyrophosphate	34.1	0.0159

*) The activity is measured in moles of diol dehydrated per gram of catalyst per hour.

These results show that a magnesium-base catalyst is not a good catalyst for dehydration of vincinal diols. In fact, it will facilitate isomerization reactions, which is not conducive to good selectivity for diolefins as it leads to production of carbonyl compounds.

For the dehydration of vicinal diols it is important that the catalyst not be acidic.

WHAT WE CLAIM IS:—

1. A process for the catalytic dehydration of vicinal diols and/or olefinic alcohols to diolefins and/or olefinic alcohols which process comprises carrying out the dehydration in the presence of a catalyst consisting of calcium pyrophosphate alone or a catalyst composition comprising (i) calcium pyrophosphate, and (ii) at least one pyrophosphate, whether mixed or not, of at least one of lithium, sodium, strontium and barium, and/or at least one neutral orthophosphate, whether mixed or not, of at least one of lithium, sodium, strontium, barium and calcium.

2. A process as claimed in claim 1 wherein the catalyst composition comprises from 40 to 80% by weight of calcium pyrophosphate.

3. A process as claimed in claim 1 or claim 2 wherein the catalyst composition comprises about 60% by weight of calcium pyrophosphate and about 40% by weight of sodium pyrophosphate.

4. A process as claimed in any one of claims 1 to 3 wherein the catalyst or catalyst composition has a macroporosity of at least 0.266 cc/g.

5. A process as claimed in any one of the preceding claims wherein the calcium pyrophosphate contained in the catalyst or catalyst composition is in the form of particles having a size range of from 0.5 to 1 mm, said catalyst having been prepared by a wet process.

6. A process as claimed in any one of the preceding claims for the catalytic dehydration of methyl-2, 3-butane-diol to isoprene, comprising passing the diol in the vapor phase, whether diluted in an inert gas or not, over calcium pyrophosphate or the catalyst composition at a space velocity per hour, measured in the liquid state, of from 0.1 to 5, at a temperature of from 250 to 600° C.

7. A process as claimed in claim 6 wherein the space velocity per hour is from 0.2 to 2.5.

8. A process as claimed in claim 6 or claim 7 wherein the temperature is from 300 to 500° C.

9. A dehydration process as claimed in any one of claims 6 to 8 wherein any olefinic alcohols produced along with the isoprene are recycled and dehydrated to isoprene.

10. A process as claimed in claim 1 and substantially as hereinbefore described in any one of the specific Examples.

11. Diolefins whenever produced by a process as claimed in any one of claims 1 to 10.

12. Olefinic alcohols whenever produced by a process as claimed in any one of claims 1 to 5 or claim 10 or as a by-product of a process as claimed in any one of claims 6 to 8.

BOULT, WADE & TENNANT.

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